AD 437376

DEFENSE DOCUMENTATION CENTER
FOR
SCIENTIFIC AND TECHNICAL INFORMATION
CAMERON STATION, ALEXANDRIA, VIRGINIA

REVIEW OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

J. J. English

April 24, 1964

North American has issued a report describing the procedures and equipment developed to test uncoated- and coated-foil gage materials up to 2700 F in vacuum and air.[1] Preliminary data for uncoated René 41 and Hastelloy X, and coated and uncoated D-36, B-66, and TZM are presented in the report. The difficulties of applying nonembrittling coatings to refractory-alloy foil are reflected in the test results.

Columbium

Recent tests conducted by Martin and Thompson Ramo Wooldridge have shown that the TRW Cr-Ti-Si coating reduces the tensile strength of D-43 at 2200 F.[2,3] TRW found that subjecting uncoated D-43 to a simulated coating thermal cycle produced about the same reduction in strength as measured for TRW-coated D-43. These results were at variance with the Martin data; however, differences in strain rates make direct comparison difficult. Both investigators found that the Pfaudler coating did not greatly affect the 2200 F strength of D-43. (Note: One major procedural difference is that the Pfaudler coating is applied at a lower temperature than the TRW coating.) Martin reported that the properties of columbium alloys Cb-752 and C-129Y were essentially unaffected by the TRW coating.

Tensile tests conducted at TRW on Pfaudler- and TRW-coated B-66 showed very little effect of the coatings on yield strength up to 1600 F.[3] From 1800 to 2600 F the yield strength of Pfaudler-coated B-66 was reduced a maximum of 4000 psi. An average yield-strength reduction of about 7000 psi was measured for TRW-coated B-66 in this temperature range.

Creep testing of Pfaudler- and TRW-coated D-43 and B-66 in air is nearing completion at TRW.[3] Tests conducted to date have demonstrated that at 2000 F,

(1) Pfaudler-coated B-66 is slightly more creep resistant than TRW-coated B-66
(2) Pfaudler-coated D-43 is considerably more creep resistant than TRW-coated D-43
(3) Pfaudler-coated B-66 is slightly more creep resistant than Pfaudler-coated D-43
(4) TRW-coated B-66 is much more creep resistant than TRW-coated D-43.

The oxidation life of the coatings does not appear to be a limiting factor in creep tests at 2000 F. At 2300 F, the Pfaudler-coated alloys also showed somewhat better creep resistance. However, exposures in excess of 30 hours at 2300 F for Pfaudler-coated B-66 and 48 hours for Pfaudler-coated D-43 resulted in failure by coating oxidation.

Comparative evaluation of coated refractory-alloy sheet is continuing at the University of Dayton.[4] Summarized below are the recent bend-test results for coated 20-mil B-66 alloy.

Coating System	4T Bend Transition Temperature[(a)], F
Uncoated B-66	Below -50
TRW Cr-Ti-Si (Batch 1)	50 to 75
TRW Cr-Ti-Si (Batch 2)	125 to 150
Pfaudler silicide	275 to 325
GT&E slurry silicide	50 to 75
Chance-Vought modified silicide	450 to 500
Chromizing-modified silicide	
(Batch 1)	115 to 150
(Batch 2)	75 to 115
Boeing fluidized-bed silicide	-50 to -25

(a) The lowest temperature at which a 90° bend can be formed about a radius four times the sheet thickness.

As indicated, the Boeing fluidized-bed silicide coating was the least detrimental to bend ductility of the B-66 substrate. Cyclic-oxidation-test results for Pfaudler and TRW-coated B-66 are given below.

Coating	Test Temperature, F	Life of Coating, hours
TRW	1600	>18
Pfaudler	1600	>18
TRW (Batch 1)	2400	67 to >103
TRW (Batch 2)	2400	55 to >107
Pfaudler	2400	13
TRW (Batch 1)	2600	18 to 47
TRW (Batch 2)	2600	14 to 34
Pfaudler	2600	9 to 22
TRW	3000	<1
Pfaudler	3000	<1

Two batches of specimens were coated by TRW to give an indication of process reproducibility.

Solar is developing coating-repair methods in conjunction with their foil-evaluation program.[5] In initial tests, slurry-applied coatings have demonstrated the potential for protecting B-66 foil for 15 hours at 2500 F. The slurries consist of mixtures of metal powder and NaF activator in an organic vehicle. They are applied to the surface by painting or dipping. They are then dried and heated in an argon atmosphere. The best results to date were obtained by using a double coating cycle in which a silicon + NaF slurry is applied over a dried and diffused Cr-Ti or Cr-Ti-V layer.

Standard Pressed Steel is evaluating refractory metal fasteners for use at high temperatures.[6] An electrophoretic adaptation of the TRW Cr-Ti-Si coating is to be used to protect columbium alloys from oxidation. A $CbCr_2$ diffusion barrier will first be formed on the fastener by electrophoretic deposition of chromium followed by a diffusion anneal. Mixtures of $CrSi_2$ and $TiSi_2$ will then be deposited over the $CbCr_2$ to form the Cr-Ti-Si coating.

Molybdenum

Pfaudler reported the following oxidation test results for their PFR-6 coating on 30-mil TZM sheet.[7]

Test Temperature, F	Type of Test	Average Life, hours	95 Per Cent Confidence Range, hours
2000	Torch[a]	>150	--
2000	Furnace	(b)	--
2400	Torch[a]	57.7	32.1 to 77.4
2400	Furnace	92.7	35.9 to 149.5
2600	Torch[a]	24.8	9.6 to 40.0
2600	Furnace	21.3	3.0 to 39.6
2800	Torch[a]	5.3	0.9 to 9.7
3000	Torch[a]	1.4	0.7 to 2.2

(a) Uncorrected optical temperature.

(b) Individual lives: 28, 90, 104, >150, >150, >150 hr.

Good agreement was observed between the torch tests, which evaluate a limited coating area, and the furnace tests. Pfaudler found that shorter coating lives were obtained in furnace tests when the PFR-6 coating was applied to 10-mil TZM sheet.

Tantalum

Silicide-coating studies at Solar have again illustrated that the alloy Ta-30Cb-7.5V is more readily protected than Ta-10W[8]. The best performance was obtained with a Ti-, Cr-modified silicide coating on the vanadium-containing alloy; coating life was 22 hours at 2700 F. The maximum life for a modified silicide coating on Ta-10W at 2700 F has been 6 hours. Coating lives in excess of 60 hours at 1800 F are common for siliconized Ta-30Cb-7.5V.

Development of protective coatings for tantalum-base alloys for temperatures above 3000 F is continuing at Solar[8] and Illinois Institute of Technology[9]. IIT has achieved 10 minutes' oxidation protection of Ta-10W at 3700 F through the formation of a Ta-Hf alloy surface on the substrate. The Ta-Hf surface was produced by applying a HfH_2 slurry then fusing at a temperature slightly above the melting point of hafnium.

REFERENCES

(1) Root, D. C., and Savage, C. H., "Determination of Mechanical and Thermophysical Properties of Coated Refractory and Superalloy Thin Sheet", Technical Documentary Report No. RTD-TDR-63-4068, prepared under Air Force Contract AF 33(657)-9416 at North American Aviation (November, 1963).

(2) Appendix C, unclassified Appendix of Interim Progress Report No. 3, for period December 1, 1963, to February 29, 1964, Advanced Structural Concepts Experimental Program, Martin Company, AF 33(657)-11539.

(3) Warmuth, D. B., et al, preliminary information under a Navy Contract (February 1, 1964).

(4) Wurst, J. C., and Cherry, J. A., preliminary information under an Air Force Contract (December 13, 1963).

(5) Moore, V. S., and Stetsen, A. R., preliminary work under an Air Force Contract (January 20, 1964).

(6) Gowen, E. F., and Ortner, M., preliminary work under an Air Force Contract (November 4, 1963).

(7) Payne, B. S., et al, preliminary work under an Air Force Contract (February 15, 1964).

(8) Ohnysty, B., et al, preliminary work under an Air Force Contract (March 20, 1964).

(9) Lawthers, D. D., Rausch, J. J., et al, preliminary work under an Air Force Contract (February 14, 1964).